SCIENCE FOR CERAMIC PRODUCTION

UDC 666.321

USE OF KAOLINS FROM DIFFERENT DEPOSITS IN THE PRODUCTION OF FINE CERAMICS

G. N. Maslennikova,[1] N. F. Solodkii,[1] M. N. Solodkaya,[1] and A. S. Shamrikov[1]

Data on the mineral, chemical, and granulometric compositions of Russian kaolins used in the production of fine ceramics are summarized. The possibilities of improving the quality of ceramic mixtures for molding and slip casting based on various kaolins are considered.

The main component of fine-ceramics mixtures that has a significant effect on their technological properties is kaolin. It is a monomineral rock (despite the presence of certain impurities), since its argillaceous material consists mainly of one mineral, namely, kaolinite $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. The properties of any kaolin include low plasticity and high refractoriness. The melting temperature of kaolin varies within 1725 – 1790°C.

The main sources of kaolin for the ceramic industry are the Prosyanovskoe, Glukhovetskoe (Ukraine), Kyshtymskoe, Yeleninskoe, and Zhuravlinyi Log (Russia) deposits. Some companies use Polozhskoe, Ekaterinosvkoe, Dubrovskoe, Novoselitskoe and Vladimirskoe kaolins from Ukraine, Nev'yanskoe and Chalganskoe kaolins (Russia) [1 – 4]. The main technological requirements imposed on kaolin include homogeneity of its chemical compositions and insignificant fluctuations in its content of impurities.

Depending on the chemical composition of impurities, kaolin is classified as pure kaolin containing not more than 6% (here and elsewhere mass content) quartz and not more than 2% alkalis,; alkaline kaolin containing up to 5 – 7% potassium and sodium oxides; silica kaolin containing up to 20% finely dispersed quartz sand impurities; alkali-silica kaolin containing simultaneously substantial quantities of quartz and alkalis; and ferrous kaolin containing over 2% iron, which imparts a yellow tint and makes this kaolin unsuitable for fine ceramics, including porcelain and faience [5 – 12].

Kaolins from each deposit have technological specifics which to a great extent depend on their dispersion and texture, i.e., on their composition and density and on the mineral composition of the finely-disperse fraction. At present the porcelain and faience industry uses mainly Prosyanovskoe kaolin. Glukhovetskoe kaolin in general has inferior purity and significantly lower plasticity, and its bending strength in the air-dry state is 0.7 – 0.8 MPa. Kyshtymskoe kaolin has high plasticity, its static bending strength in the air-dry state reaches 4 MPa, but it is perceptibly contaminated by colorant iron and titanium oxides. Zhuravlinyi Log kaolin produced by dry concentration has sufficiently high quality but unstable technological parameters, especially liquescence. Eleninskoe kaolin of dry concentration has higher whiteness and liquescence parameters but low mechanical strength in the air-dry state.

The most widely used Prosyanovskoe kaolin contains up to 1% Fe_2O_3, an unspecified amount of TiO_2, and residual coagulant in an amount significantly exceeding the admissible norms. The use of such kaolin is the main reason for the decreasing quality of finished goods, primarily their whiteness.

The deteriorating quality of supplied Prosyanovskoe and Glukhovetskoe kaolins is also observed in other parameters. Sand is not completely removed from the kaolin in concentration. Thus, the residue on a No. 0056 sieve characterizing the degree of dispersion of Prosyanovskoe kaolin reaches 0.82%, and that of Glukhovetskoe kaolin 1.32%. Note for comparison that concentration factories abroad perform the separation of sand much more thoroughly; the residue on a No. 0056 sieve ranges from 0.03 to 0.15%. In other words, certain requirements are imposed on kaolin used in fine-ceramics production, which should be obligatory for companies mining and supplying kaolin, as well as for its customers.

[1] State University of Management, Moscow, Russia; Ural'ski Farfor JSC, Yuzhnoural'sk, Russia; Keramik-Plast Company, Yuzhnoural'sk, Russia.

TABLE 1

Parameter	Deposit				
	Prosyanovskoe	Glukhovetskoe	Kyshtymskoe	Eleninskoe	Zhuravlinyi Log
Chemical composition, %:					
SiO_2	46.1 – 46.9	46.1 – 47.9	46.5 – 49.6	46.9 – 48.1	46.0 – 48.2
Al_2O_3	36.0 – 38.5	37.5 – 39.2	35.5 – 37.6	34.0 – 37.4	35.5 – 39.0
Fe_2O_3	0.3 – 0.8	0.3 – 0.9	0.5 – 1.4	0.5 – 0.7	0.4 – 0.9
TiO	0.1 – 0.7	0.1 – 0.7	0.5 – 0.6	0.4 – 0.6	0.2 – 0.4
CaO	0.1 – 1.0	0.1 – 0.5	0.1 – 0.9	0.1 – 0.4	0.2 – 0.6
MgO	0.05 – 0.1	0.0 – 0.2	0.2 – 0.3	0.1 – 0.2	0.1 – 0.2
$K_2O + N_2O$	Traces	0.6 – 0.7	0.4 – 0.9	0.3 – 0.5	0.6 – 0.9
calcination loss	13.3 – 13.9	10.5 – 11.2	12.2 – 13.7	11.5 – 13.0	13.4 – 14.1
Residue on No. 0063 sieve, %	0.01 – 0.50	0.03 – 0.05	0.04 – 0.07	0.01 – 0.05	0.01 – 0.05
Granulometric composition, %:					
fraction above 0.05 mm	0.58 – 4.72	0.30 – 0.80	0.56 – 4.05	1.63 – 1.87	1.25 – 1.90
0.05 – 0.01 mm	16.68 – 17.82	7.00 – 13.50	17.48 – 31.19	34.69 – 36.60	15.40 – 17.20
0.01 – 0.005 mm	11.07 – 12.52	14.20 – 18.90	10.38 – 15.60	14.50 – 22.10	16.11 – 19.22
0.005 – 0.001 mm	30.40 – 31.82	16.50 – 21.40	29.40 – 32.39	22.10 – 24.40	13.20 – 21.40
below 0.001 mm	35.68 – 37.74	37.20 – 59.80	30.89 – 36.16	25.10 – 35.40	37.30 – 45.60
Relative water addition, %	28 – 32	28 – 33	30 – 33	25 – 30	29 – 34
Bending strength, MPa:					
in air-dry state	0.8 – 1.4	0.6 – 0.8	2.5 – 4.0	0.5 – 0.9	2.5 – 3.5
after firing at 1380°C	80 – 100	70 – 86	90 – 120	60 – 90	90 – 110
Refractoriness, °C	1770 – 1790	1730	1730 – 1760	1750 – 1770	1750 – 1760
Absorption capacity, mg/liter	20.6	21.3	18.9	13.8	23.3
Whiteness:					
after drying at 110°C	75 – 88	91	69 – 74	75 – 84	70 – 83
after firing at 1300°C	80 – 85	75 – 90	75 – 80	79 – 87	71 – 83

Kaolin intended for making fine ceramics should satisfy the following requirements:

– color after firing in a neutral gas medium up to a temperature of 1350°C: white;

– amount of mechanical impurities (%): residue on a sieve with 4900 holes/cm^2 not more than 0.1 – 0.5; residue on a sieve with 10,000 holes/cm^2 not more than 0.8 – 1.5; iron oxide content not more than 0.6 – 0.8, titanium dioxide not more than 0.4 – 0.5; sulfuric anhydride not more than 0.2 – 0.4.

Kaolin should have a certain (stable) moisture. Fluctuations in the moisture of kaolin may cause errors in calculating the ceramic mixture composition.

It should be noted that the best grades of kaolins meet the requirements of the ceramic industry, but their production volume is, unfortunately, limited and does not fully satisfy the demand of the industry. In recent years the contrast between the increasing requirements on the quality of ceramics and the constant deterioration of the quality of kaolin, in particular, its chemical and granulometric composition, its bending strength in the air-dry state, etc., is becoming more evident.

It has been established that different product batches of concentrated kaolins, although mined at the same site of a deposit, may differ significantly in their technological properties. Apart from natural properties, these differences are related to the specifics of the concentration technologies and the colloid-chemical phenomena that are the basis for the electrolytic concentration method. This is further evidence of the fact than the majority of kaolins of the same name coming from different deposits differ sharply, although their chemical compositions are close. These specifics of kaolins impede the development of ceramic mixture formulas and replacement of one grade of kaolin by another without a preliminary correction [6 – 18].

The chemical compositions and characteristics of concentrated kaolins from various deposits are listed in Table 1.

Kaolins are used in various sectors of industry, hence, the requirements imposed on them are different. Kaolins intended for the ceramic industry should meet the requirements of GOST 21286–82. The most rigid requirements on kaolin are related to its content of colorant oxides of iron and titanium. The parameters specified in the standard do not reflect all characteristics of kaolin quality that need to be taken into account in the production of household and technical porcelain. It should be noted that foreign producers, due to their specific technology, obtain a product in which the parameters affecting the quality of the finished articles are strictly regulated. The main difference of these kaolins from the Russian and Ukrainian kaolin grades is the constancy of the physico-chemical properties of a particular grade that do not change for years, which makes it possible to stabilize the properties of slips and successfully mechanize the production of ceramic articles.

Kaolins from the Prosyanovskoe deposit produced by wet concentration have the greatest diversity of structural-

TABLE 2

Kaolin	Number of analyzed		Crystallinity index	
	samples	fractions	Hinckley	Jones – Murray
Kyshtymskoe	1	1	0.96	0.4
Eleninskoe	1	1	1.19	0.5
Zhuravlinyi Log	4	4	0.83	0.7
Prosyanovskoe	27	27	1.68 – 1.10	–
Glukhovetskoe	2	6	1.68 – 1.65	–
Sedletskoe (Czech Republic)	1	1	1.03	0.3
Xuchon (China)	1	1	1.18	0.5
English	1	1	1.07	0.5
Polish	1	1	0.73	0.5

mechanical and technological properties. Analysis of a large number of batches of Prosyanovskoe kaolin indicates that the bending strength of kaolin in the air-dry state decreases with increasing viscosity. More peptized kaolins have high mechanical strength. This is confirmed by the dependence of the bending strength on the structure formation threshold: as the latter increases, the mechanical strength grows. This is corroborated as well by the bending strength growing with decreasing filtration rate, which decreases as the structure formation threshold increases.

Kaolins from different deposits have different shapes of kaolinite crystals. Thus, Glukhovetskoe kaolin contains monocrystalline kaolinite, in which vermiform aggregates are found; kaolinite of Prosyanovskoe kaolin has the shape of large and small scales; kaolinite from Kyshtymskoe kaolin is shaped as large leaves and scales, and its fraction with particle size below 1 µm contains felt-like clusters; kaolinite of Eleninskoe kaolin has small scales with an insignificant inclusion of large scales. The diameters of these scale ranges in the limits of $0.1 – 3.0$ µm and their thickness is $0.01 – 0.03$ µm or more. The thickness of the kaolinite scale aggregates may reach $15 – 20$ µm. Research performed at the Institute of Geochemistry and Physics of Minerals of the Academy of Sciences of Ukraine (Kiev) indicates that the degree of structural ordering and the shape of kaolinite particles are the most important characteristics of kaolin properties. Kaolinite particles may be rather satisfactorily crystallized.

A comparison of the characteristics of Prosyanovskoe and Kyshtymskoe kaolins performed by the Republican Engineering-Technical Center of Powder Metallurgy (city of Perm) established that Prosyanosvkoe kaolin typically has

clearly delineated particles approaching the hexagonal shape typical of traditional kaolinite. Kyshtymskoe kaolin contains tubular particle usually referred to halloysite that retain their structure after calcination at a temperature of 900°C [14, 15].

X-ray and electron-diffraction studies performed at the NIIF institute (St. Petersburg) show that kaolins differ perceptibly in the perfection (ordering) of the crystal structure of kaolinite. The differences in the ordering of the crystal lattice of kaolinite are responsible for certain modifications in the diffraction patterns. In the case of a more ordered structure where the elementary layers are regularly packed, the x-ray reflections are sharp, well resolved, and numerous; in the case of a less ordered structure where the elementary layers are shifted with respect to each other, or turned, etc., few diffuse and poorly resolved reflections are registered.

The indexes of the degree of crystallinity of kaolinite determined by the Hinckley and Jones – Murray methods in kaolins used in the ceramic industry are listed in Table 2.

Analysis of the crystallinity indexes of the kaolins used in the domestic industry shows that the majority have a relatively high degree of ordering of the crystal structure and rather high values of the Hinckley crystallinity index.

It can be seen from Table 3 that as the degree of crystallinity of kaolins grows, the energy of dehydration increases, which points to the possibility of the dehydration process extending and shifting to a higher-temperature range (the latter may lead to the formation of defects in ceramics).

The studies indicate that well-crystallized kaolins sinter faster than weakly crystallized materials. The kaolins sintering at relatively low temperatures making part of porcelain mixtures increase the quantity of defective products after the second firing due to an increased number of defects (pinholes, blisters).

Analysis of the differential-thermal curves of kaolins in heating reveals the nonuniform energy costs of the process of dehydration of kaolins in the range of the second endothermic effect that is determined by the removal of constitution water. The insignificant rate of this process leads to the formation of such common glaze defects as pinpoints.

Kaolins that have different degrees of crystallinity also differ in their colloid-chemical properties, in particular, the methylene blue adsorption index. This index is commonly used to characterize the quality of kaolins and plastic refractory clays, as well as in the calculation of porcelain mixture compositions.

To characterize the specific surface area of kaolins, one determines its capacity for methylene blue adsorption, whose

TABLE 3

Parameter	Kaolin					
	Alekseevskoe	Prosyanovskoe, sample 1	Glukhovetskoe	Prosyanovskoe, sample 2	Prosyanovskoe, sample 3	Prosyanovskoe, sample 4
Hinckley crystallinity index	0.93	1.10	1.34	1.40	1.50	1.60
Activation energy, kJ/mole	94.37	98.55	105.66	107.66	112.27	113.65

value agrees with the degree of dispersion of the kaolin. Thus, finely dispersed kaolins have the highest index of 12 – 18 mg/g; for some kaolins it reaches 28 mg/g. The increased adsorption index in kaolins is determined by their granulometric composition. As the adsorption index of the kaolin increases, its dispersion increases, or finely dispersed impurities of low-melting minerals, such as montmorillonite, are formed, or the former and the latter occur simultaneously with growing sintering intensity. This information gives comprehensive information on the properties of kaolin. Research carried out at the NIIF institute established a correlation between the mechanical strength of kaolin in the air-dry state and its adsorption index.

V. V. Glasson corroborated that kaolins with high indexes of methylene blue adsorption from aqueous solutions, as a rule, have high (air and total) shrinkage and mechanical strength of samples in the air-dry state. Note that kaolins with an adsorption index in the interval of 9 – 12 mg/g are the most suitable for slip casting and kaolins with an adsorption index over 12 mg/g are optimum for plastic molding. When using kaolins with an adsorption index below 9 mg/g, the mixture composition has to be corrected.

For the calculation of ceramic mixture compositions it is convenient to use another parameter, namely, the kaolin number characterizing the degree of dispersion of the argillaceous component. This number represents the ratio of the kaolinite introduced with kaolin to the total content of kaolinite in the mixture. For instance, the number 75% means that the mixture contains 75% relatively coarsely-dispersed kaolinite introduced with kaolin and 25% finely-dispersed kaolinite introduced with clay. A decrease in the kaolin number correlates with a more compact packing of particles in the mixture and a more intense sintering process.

In the beginning of kaolin heating the adsorbed and interlayer water is the first to be removed, which is accompanied by the first endothermic effect (120°C). This effect corresponds to rather high weigh losses, due to dehydration of mica. In the temperature interval of 400 – 600°C the constitution water is removed, which is registered on the differential thermal curves as the second endothermic effect. Simultaneously with water removal, the crystal lattice of the argillaceous minerals (kaolinite, hydromica) is destroyed and the article volume decreases (shrinkage). The process is accompanied by losing approximately 6 wt.%. The shrinkage under the exothermic effect in Glukhovetskoe and Zhuravlinyi Log kaolins exceeds the shrinkage of Prosyanovskoe and Kyshtymskoe kaolins, which is due to their higher kaolinization and the lower content of impurities in the form of quartz grains, feldspar, etc. At a temperature above 600°C complex transformations take place in kaolins and they interact with other components of the ceramic mixture. The first endothermic effect occurs and ends sooner in Prosyanosvkoe (910 – 990°C) and Kyshtymskoe (910 – 970°C) kaolins compared to Glukhovetskoe (975 – 1070°C) and Zhuravlinyi Log (980 – 1000°C) kaolins.

In calcination (900 – 1000°C), chemically bound water and carbonic acid contained in the carbonates are removed from kaolins, furthermore, organic impurities and sulfur burn out. The weight loss in calcination of kaolin with an insignificant content of organic compounds and the usual quantity of impurities depends mainly on the content of the argillaceous component. Therefore, calcination losses, which can be determined fast enough, are used to indirectly infer the amount of kaolinite in the kaolin and, accordingly, the content of alumina.

Kaolin calcined at 1000°C has approximately the same effect on the porcelain mixture as grog additives or the coarse fraction of non-calcined kaolin. The difference is manifested in the intensity of the effect of grog components: the lowest is the effect of the coarse fraction and the most intense effect is exerted by calcined kaolin.

The calcination of kaolin at relatively low temperatures (450 – 750°C) shows that its hydrophilic properties can change with time. The intensity of these properties is in inverse proportion to the calcination temperature. The beginning and end of the second exothermic effect have a certain tendency to decreasing in Prosyanovskoe (1115 – 1175°C) and Kyshtymskoe (1150 – 1180°C) kaolins compared to Glukhovetskoe (1225 – 1265°C) and Zhuravlinyi Log (1220 – 1250°C) kaolins.

Thus, the thermal analysis corroborates the fact that Zhuravlinyi Log and Glukhovetskoe kaolins are purer than Prosyanovskoe and Kyshtymskoe kaolins.

In heat treatment of natural and concentrated kaolin from the Zhuravlinyi Log deposit, the formation of primary mullite is registered (in x-ray patterns) starting with a temperature of 1050°C and reaches a higher intensity at 1200 – 1250°C. The secondary mullite is formed at 1200 – 1300°C. At higher temperatures mullite becomes recrystallized.

The water absorption of kaolin samples fired at 1350°C is an important factor determining the suitability of kaolin for the production of fine ceramics (degree of sinterability, refractoriness).

The water absorption of Prosyanovskoe kaolin samples fired at 1350°C is related by a complex multifactor dependence to the mineral composition of kaolin (the quantity of potassium feldspar and mica materials), which shows that it is hard to control the water absorption process in the production of kaolin since the process of concentration of the initial material is not directed to the formation of a monomineral potassium component but only to its separation by grain sizes, i.e., the argillaceous and the sand components. Consequently, it is advisable to determine the quality of kaolin not based on its water absorption but based on the weight part of Al_2O_3 with the norm exceeding 36%. The introduction of this norm would prevent the supply of alkaline kaolins, whose water absorption is not more than 6% (although this parameter does not characterize the sinterability of kaolins).

Mechanical impurities, mainly free quartz sand in the form of rather large grains and residual impurities of non-decomposed mineral rocks, significantly decrease the plas-

ticity of kaolins, which has a negative effect on the plasticity of ceramic mixtures. Furthermore, large impurity particles disturb the homogeneity of mixtures and raise their sintering temperatures. It is known that an excessive content of calcium, magnesium, iron, sodium, and potassium compounds decrease the refractoriness of kaolins. The presence of more than 1.5% mechanical impurities indicates a poor quality of kaolin concentration.

The undesirable impurities in kaolin are carbonates and sulfates, which in firing release CO_2 and SO_3 and thus produce interior cavities in the ceramic material impairing the electric and mechanical properties of technical and household porcelain. Moreover, increased porosity and swelling of a ceramic material can be caused by organic impurities contained in the mixture in excessive quantities.

The presence of sulfuric anhydride in kaolin is an indicator of iron impurities in the form of pyrite FeS_2, whose effect on the quality of porcelain and faience articles may be manifested in firing at a temperature of $1000 – 1250°C$. The content of sulfuric anhydride SO_3 in Prosyanovskoe kaolin varies within the limits of $0.07 – 0.24\%$.

The suitability of kaolin as the main component of ceramic mixtures depends, on the one hand, on the technical properties of kaolin suspensions and the plasticity of the ceramic mixture and, on the other hand, on the properties of the fired material. Kaolin imparts a lower plasticity to ceramic mixtures than clay does, but the absence of undesirable impurities in the kaolin composition provides for the required whiteness of the ceramic material and prevents the deformation of the product in firing. Note also that kaolin in a porcelain mixture acts as a crystal-forming component creating the crystalline phase, namely, mullite $3Al_2O_3 \cdot 2SiO_2$, in firing.

The chemical and mineral compositions of kaolin determines its refractoriness, mechanical strength, thermal stability, moisture resistance, and other properties of ceramic materials, which is responsible for the reliability, stability, and longevity of ceramic articles under various service conditions. Thus, as the content of alumina Al_2O_3 that has a substantial share in the chemical composition of kaolin increases, the refractoriness and mechanical strength of ceramics grow. Silica SiO_2, which is also present in kaolin in substantial quantities, on the one hand, lowers the plasticity and shrinkage of the ceramic mixture and (improves its drying and firing conditions), and on the other hand, decreases its refractoriness.

The impurities of iron and alkali metal oxides contained in kaolins (Fe_2O_3, Na_2O, and K_2O) contained in kaolin have a negative effect on the properties of radio ceramics and electric porcelain materials. The presence of excessive quantities of iron and titanium oxides in kaolin impart a certain tint (yellow or bluish) to porcelain and faience. Furthermore, if kaolin contains free iron, it may show up on the surface of the product in the form of dark dots. The research of the NIIF established that increasing the total sum of the colorant ox-

ides ($Fe_2O_3 + TiO_2$) in a porcelain material just by 0.1% decreases its whiteness by approximately 3%.

Iron and titanium oxides are intense fluxes decreasing the viscosity of the liquid phase and the sintering interval of ceramic materials; furthermore, they lower their mechanical strength. Calcium oxide, frequently found in kaolin, is a flux as well. The negative effect of this oxide is also manifested in deteriorating structural-mechanical properties of kaolin, namely, enhanced instability and decreased slip fluidity and liquescence.

The content of CaO in kaolin prescribed by the state standards and technical conditions is limited to 0.8%. However, the use of milk of lime with a decreased reaction capacity, i.e., with $40 – 50\%$ CaO content instead of $80 – 90\%$ prescribed by technical regulations, leads to its excessive introduction (nearly three times more) in the course of coagulation of the kaolin suspension and, consequently, to increasing pH, decreasing structure formation threshold, and deteriorating flow properties. Finally, it has a negative effect on the porosity and electrophysical parameters of electrotechnical porcelain. The use of the electrolyte-free method for kaolin concentration makes it possible to decrease the pH to 6.5 or lower and decrease the content of CaO.

The storage of kaolins in closed premises for $2 – 3$ months facilitates the transformation of active lime $Ca(OH)_2$ into calcium carbonate $CaCO_3$ and perceptibly decreases its negative effect.

Kaolins produced by moist concentration using electrolytes are characterized by their elasticity index, structure formation threshold, instability, and active alkalinity (pH) of kaolin suspension.

The elasticity of kaolin particles has a great effect on the formation of a plastic mixture that changes its shape under pressure without disrupting its continuity and retains this shape after the load is removed. Kaolins are divided into three groups with respect to their elasticity level: group 1) elasticity index below 0.05, group 2) from 0.05 to 0.04, and group 3) over 0.40.

Moist-concentrated kaolins whose elasticity limits are equal to $0.01 – 0.05$ are characterized by sufficient elasticity and a low yield point. Preforms (intermediate molded pieces) based on slip containing such kaolin have high mechanical strength and low residual moisture. In using wet-concentration kaolin with elasticity equal to $0.1 – 0.4$, an increased quantity of defects (notches, cracks) is observed.

Instability is most frequently observed in kaolins produced by electrolyte concentration, in which excessive alkalinity has been neutralized before dehydration. It is found that the maximum instability corresponds to the optimum liquescence of kaolins.

The instability of kaolins can be lowered by adding coagulants into the kaolin suspension (for instance, milk of lime, calcium chloride, or calcium sulfate). The use of kaolins with an instability index of 15 or more causes instability in porcelain mixtures and hampers molding of articles. Such a state of kaolins depends on the structure of the surface layer of

TABLE 4

Technological group	Density, g/cm^3	Elasticity index, g/cm^3	Structure formation threshold, g/cm^3	Instability	pH	Slip characteristics
First	1.365 – 1.350	< 0.05	> 1.36	> 15	> 9.0	Prone to crack formation under increased liquescence
Second	1.760 – 1.365	0.05 – 0.40	1.28 – 1.36	12 – 15	8.5 – 9.5	Have normal properties
Third	> 1.760	> 0.40	< 1.28	< 12	< 8.5	Are hard to liquefy, require an increased amount of water

kaolin particles determined by the properties of the adsorbed ions, whereas the scale shape of kaolin particles determines the instability of kaolins. Therefore, when kaolins are used in the production of fine ceramics, it is necessary to introduce highly plastic clay additives acting as binders or kaolin concentrated using hydrocyclones.

It was shown in the studies of V. V. Glasson that the method for determining the elasticity index is sensitive only for the second-group kaolins, and for kaolins of the other groups one should determine the structure formation threshold, i.e., the density at which the elasticity of the kaolin suspension disappears. Note that V. V. Glasson found a dependence between the structure formation threshold, instability, and pH of kaolins of different groups. The relative technological properties of different groups of kaolins are listed in Table 4.

The most suitable for porcelain production are kaolins of the second group, which easily liquefy, form suspensions with normal viscosity and thickening, uniformly dehydrate, and have low instability. The optimum technological properties are found in kaolins that form a suspension of density 1.55 – 1.60 g/cm^3 (according to an areometer).

However, in most cases the Prosyanovskoe Concentration Works, as a rule, supplies kaolins of the first group. This depends not only on excessive water glass added to the kaolin in the course of moist concentration, but also on the increased temperature of drying kaolin cakes. In this case the elastic properties of kaolin suspensions containing a relatively small water glass additive sharply deteriorate. The deterioration of elastic properties to a lesser extent is also observed in dry-concentration kaolins produced without electrolytes.

An excess of coagulating electrolytes contained in concentrated kaolins requires an increased water content in the preparation of molding mixtures and casting slips. An excessive quantity of peptizing electrolytes in kaolin causes stratification of filter-pressed cakes and increases instability of the mixture.

The quality of kaolin of the first group is corrected by adding hydrochloric acid in a quantity calculated by titration with 0.5 N solution of hydrochloric acid. Coagulants decrease the mechanical strength of ceramics, especially when introduced into kaolin in excessive quantities.

It is established that slip based on kaolin with a predominant amount of the residual peptizer contains excessive elec-trolyte, which delays the process of article formation. The preform becomes more brittle, which causes the formation of numerous notches and even cracks. Slip based on kaolin with the prevailing quantity of residual coagulant is hard to liquefy and requires additional moisture content, which prolongs and complicates the production process. Slip containing an excess of coagulating electrolytes is not recommended for porcelain production as it is difficult to stabilize the properties of slip in industrial conditions. It is advisable to use kaolins that do not manifest elastic forces (pycnometric density 1.28 – 1.36 g/cm^3).

To improve the casting properties of slip and decrease the quantity of electrolytes, the slip is subject to filter-pressing.

Slip of satisfactory quality based on kaolin with the prevailing quantity of residual coagulants is characterized by thickening number 1.4 and density 1.61 – 1.62 g/cm^3 (by an areometer) with introduction of 0.25 – 0.40% water glass and 0.10 – 0.15% soda. The introduction of electrolytes (soda, trisodium phosphate, sodium pyrophosphate, concentrated distiller grain slops, and sodium and aluminum ligno-sulfonates obtained from this concentrate) into a porcelain mixture decreases the working water content and increases the mechanical strength of dried samples of kaolin and porcelain mixtures. The process of molding from a mixture containing 0.5% sodium lignosulfonate is much easier than from a mixture not containing additives.

Since highly dispersed clays and kaolins have an enhanced activity in the presence of electrolytes, the purity of water used in slip preparation is of special importance. Using distilled water, one can obtain slip with satisfactory properties. However, they frequently exhibit undesirable properties when using hard water. For highly dispersed and dispersed kaolins the additives used for liquefying are usually water glass and sodium pyrophosphate; for coarsely-disperse kaolin the additives are soda, as well as tannin and lignin.

The presence of soluble salts in concentrated kaolins has a negative effect on the properties of porcelain and faience mixtures containing these kaolins and on the quality of finished products. This negative effect is especially evident in casting. The presence of soluble sulfates in a ceramic slip decreases the liquefying capacity of water glass. To obtain a slip with sufficiently satisfactory casting properties, it is necessary to introduce an increased quantity of electrolytes, which has a negative effect on the technological properties of

TABLE 5

Kaolin	pH	Content of ions in aqueous extract, mg · eq per 100 g of material						
		Ca^{2+}	Mg^{2+}	K^+	Na^+	OH^-	Cl^-	SO_4^{2-}
Glukhovetskoe	7.55	0.38	0.12	0.08	0.16	0.20	0.40	0.23
Prosyanovskoe	7.85	1.02	1.60	0.32	1.05	0.88	0.86	2.20
Kyshtymskoe	9.20	0.80	0.38	0.09	0.39	1.20	0.40	0.23
Zhuravlinyi Log	8.30	0.80	0.38	0.03	0.45	0.88	0.40	0.60

slip and the quality of cast preforms. Thus, is becomes difficult to cast products in gypsum molds, the number of rejected products grows, and the amount of broken preforms grows as well, due to the brittleness and low mechanical strength of the products.

The content of soluble calcium and magnesium salts in an aqueous extract has a direct effect on the liquescence of kaolin and the flow properties of slips. The data on the content of soluble salts in kaolins from different deposits are shown in Table 5.

It is established that Glukhovetskoe and Prosyanovskoe kaolins contain soluble salts significantly deteriorating the casting properties of slips. Practice shows that, in aging, the properties of kaolin homogenize, and soluble salts are partly removed as the result of hydrolysis and their transformation into insoluble compounds.

The quality of casting slip is influenced by pH, which depends on the content of soluble salts. Considering that kaolins create an acid medium causing perceptible complication in the production of porcelain and faience slips, the pH of kaolin in the production process should be maintained at 7.5 – 9.5. Thus, for pH within the limits of 9.6 – 10.9 in a faience mixture and 9.9 – 10.5 in a semiporcelain mixture an increase amount of electrolyte is required for liquefying. Such slip rapidly thickens, and only introduction of a sodium pyrophosphate additive and increased moisture make it possible to obtain satisfactory casting properties.

It is established that the optimum pH value for low-temperature porcelain is 8.8 – 9.0, for faience 8.9 – 9.3, and for household porcelain 8.0 – 9.5; the content of soluble calcium and magnesium salts is 0.081 – 0.084 mg · eq/liter, and the admissible content of chlorides (NaCl) in the slip is 1.5 – 2.5 mg · eq/liter.

The practice of many companies corroborates the fact that sulfates pass completely into an insoluble state upon introducing $Ba(OH)_2$ or $BaCO_3$. An excess of barium carbonate, similar to an excess of barium sulfate, impairs the casting properties of the slip and the preform quality, therefore, the proportioning of barium compounds should correspond precisely to the content of sulfates in the slip.

Many manufacturers using Prosyanovskoe kaolin calculate the amount of the peptizer (water glass) added to a porcelain mixture intended for thin-walled articles taking into account the elasticity of kaolin. Thus the Riga Porcelain Works set the quantity of water glass to be introduced depending on the pH of the kaolin. For instance, the pH of the

kaolin casting suspension was equal to 8.9 – 9.5. The introduction of an optimum quantity of water glass makes it possible to stabilize the properties of casting slip and to improve the preform quality. In the Stroipolymerkeramika Company (Kaluga Region) the casting properties of the slip based on Zhuravlinyi Log kaolin are regulated based on the pH of the suspension.

The long-time research of Prosyanovskoe kaolin established a correlation between its deflocculation (liquescence) and the concentration of coagulating electrolytes: when the concentration increases, the deflocculation processes is impeded. Insignificant fluctuations in the cation exchange capacity of kaolin in the limits of 2.8 – 4.7 mg · eq per 100 g has little effect on its deflocculation process. If the cation exchange capacity of kaolin reaches 7 mg · eq per 100 g, to ensure deflocculation, one should raise the water content substantially, in addition to introducing electrolytes. The kaolin deflocculation regularities also hold for porcelain and faience slips. At the same time, the content of coagulating cations and anions in kaolin has a smaller effect on the deflocculation of the faience slip than on porcelain slip, since the kaolin content in the former is higher than in the latter.

The studies performed by A. P. Pyzhova (NIIF) corroborated the need for porcelain and faience factories to procure kaolins meeting certain requirements regarding their main colloid-chemical characteristics, such as cation exchange capacity, dispersion, and content of soluble salts, which should be minimum (ought to be standardized). It should be noted that the content of soluble salts is one of the most important parameters of the casting properties of kaolins. It is recommended to determine this content using the fast method developed at the NIIF.

The stability of the granulometric composition of kaolin in preparing ceramic mixtures and molding preforms is important as well, since a constant packing of mineral particles stabilizes the shrinkage of articles in firing. The instability in granulometric composition of kaolin is accompanied by instability in the process of preparing porcelain mixtures and the process regimes and, consequently, an increased amount of defective pieces. The insufficient amount of data on the granulometric composition of kaolins does not yet permit prescribing its standard parameters.

The ratio between kaolin and clay in a ceramic mixture should provide the required degree of dispersion and, accordingly, its cohesion, plastic strength, and casting properties. The degree of dispersion of a ceramic mixture is estimated

TABLE 6

Kaolin	Content of particles, %, of size, mm				
	0.25 – 0.05	0.05 – 0.01	0.01 – 0.005	0.005 – 0.001	below 0.001
Prosyanovskoe:					
moist concentration	0.6 – 4.7	16.0 – 18.0	11.0 – 13.0	30.0 – 32.0	30.0 – 37.0
dry concentration	7.4	25.9	11.3	28.6	26.7
Glukhovetskoe	0.4 – 0.7	7.2	14.5 – 19.0	16.0 – 21.0	49.0 – 59.0
Kyshtymskoe	0.8 – 1.0	18.0 – 27.0	40.0 – 50.0	12.0 – 14.0	17.0 – 18.0
Zhuravlinyi Log	–	21.4 – 32.0	13.3 – 19.6	21.5 – 37.8	37.3 – 45.6

based on the content of the fraction with particle size not greater than 1 μm. The content of this fraction in the kaolins used in the domestic ceramic industry is distributed as follows (%): 58 – 65 Glukhovetskoe kaolin, 38 – 40 Prosyanovskoe, 19 – 23 Kyshtymskoe, 33 – 58 Zhuravlinyi Log. The granulometric composition of some grades of kaolin is listed in Table 6.

The use of finely milled kaolin (particle size below 2 μm) in a porcelain mixture nearly doubles its bending strength in the air-dry state and increases the raw material density and the mixture plasticity.

The granulometric composition of kaolin is diverse. The finely disperse part of kaolin with particle size not more than 1 μm is the most active. The content of particles below 1 μm varies from 15 to 55%. The optimum quantity of the fraction with particle size below 1 μm for a faience mixture is 28 – 37% and for a semiporcelain mixture and low-temperature porcelain 28 – 32%. When the content of this fraction is over 40%, the duration of the article wall formation increases and simultaneously the amount of waste grows (a broken spout, broken walls, and other defects). With 20 – 25% content the height formation period shortens, but the number of defective articles grows as well (cracks, notches, etc.).

A study of the morphology of particles whose size did not exceed 1 μm in various samples of Prosyanovskoe and Kyshtymskoe kaolins before and after chemical concentration revealed the following regularities. Particles of different kaolin samples taken from the same deposit differed in shape, size, thickness, and degree of crystallization. Thus, particles of Prosyanovskoe kaolin have better crystallinity than particles of Kyshtymskoe kaolin. As the depth of sample taking increases, the average size of kaolin particles grows.

A modification of the size of kaolinite particles makes it possible to regulate the technological properties of kaolin and ceramic mixtures. For this purpose one should fractionate the initial kaolin and then deliver kaolin batches of particular fraction compositions depending on the consumer's demand.

It is established that the properties of porcelain mixtures in the slip-like, plastic, and air-dry states differ sharply depending on the fractional composition of kaolin. The size of kaolinite particles has a significant effect on the behavior of porcelain mixtures not only before firing but during firing as

well. The particle size also affects the formation of the structure of material in the air-dry state, which to a great extent determines the processes under heat treatment. Thus, coarse-disperse kaolin produces mixtures with a porous air-dried structure (with an identical mineral composition and equal dispersion of the grog components). The introduction of finely dispersed kaolin makes the structure of the ceramic mixture in the air-dry state more compact.

Finally, the fire shrinkage, the degree of deformation of samples in firing, the sintering temperature, translucence, and mullitization depend on the porosity of the material in the air-dry state. Materials containing a finely-disperse kaolin fraction have lower fire shrinkage and lower translucence when fired at the optimum temperature. When a coarsely-disperse fraction is used, the specified parameters change in the reverse order.

Porcelain mixtures containing only the kaolin fraction with particle size below 2 μm differ sharply in their qualities from mixtures containing the fraction with particle size over 2 μm, their chemical and mineral compositions being identical. A similar effect of the specified kaolin fractions is observed as well in porcelain mixtures (in the slip-like, plastic, and air-dry states).

The technological properties of a porcelain mixture based on finely-disperse kaolin (particle size below 2 μm) differ sharply from the properties of a mixture containing kaolin with particle size ranging from 2 to 60 μm. The fine kaolin fraction produces thick low-mobility slips and the molding mixtures having high plasticity and mechanical strength in the air-dry state. The coarse kaolin fraction yields mobile slips, unstable molding mixture, and samples with low mechanical strength in the air-dry state. Ceramic mixtures containing finely-disperse kaolin particles have an increased sintering interval and high resistance to deformation.

The investigation of slips containing highly dispersed plastic clays and kaolins demonstrated that the specific surface area of the disperse phase in such slip gradually decreases with time and after some months its value approaches the specific surface area of clay (kaolin) dispersed by the traditional method (propeller mixer). However, even after a month of storage the slip based on highly dispersed clays and kaolin produces preforms of higher quality than preforms cast from slip prepared from clay and kaolin dispersed by the traditional method.

The mechanical strength of concentrated kaolin has a perceptible effect on the quality of ceramics and decreases the number of rejected products. However, the technology of concentrating kaolin used at concentration factories does not provide for controlling its mechanical strength.

The integrated study of the effect of different factors on the mechanical strength of kaolin carried out at the VNIInerud Institute (Tol'yatti) demonstrated that, for mono-mineral kaolin, it depends on the degree of ordering of the crystal lattice of kaolinite, the shape of particles, the dispersion composition, and the specific surface area, and for polymineral varieties it depends as well on the presence and quantity of argillaceous materials (mixed-layer, hydromica, montmorillonite, etc.). The relation of the strength of kaolin to its specific surface area is the closest, which indirectly corroborates the above-mentioned set of factors that influence the physicochemical properties of kaolin.

Kaolin with a preset strength level can be obtained by mixing kaolins from different deposits, since in most cases a significant factor, apart from strength, is its chemical composition. Thus, the strength of kaolin can be increased 1.5 – 2.0 times by introducing 20 – 30% fractionated alkaline or gneiss kaolins. Intense mechanical mixing of a kaolin paste or suspension or, especially, a mixture of kaolins contributes to raising its strength.

The maximum effect in strength growth is observed in kaolin mixtures containing montmorillonite or hydromica. It is believed that under protracted mixing an intermolecular interaction between particles of kaolinite and montmorillonite takes place, which leads to the formation of a stronger structure. The introduction of 0.05% urea and 0.02 – 0.04% urea mixed with sodium carbonate followed by thorough mixing increases the mechanical strength of kaolin by 2.2 – 3.9 times. Accordingly, the number of rejected products decreases.

In order to impart strictly regulated properties to a ceramic mixture, it is advisable to perform mixing and homogenization of several types of kaolin from different deposits that have a similar mineral composition but differ significantly in their granulometric compositions; therefore, being mixed, they facilitate the averaging of properties.

Several factories producing sanitary and building ceramics, household porcelain, and faience use mixtures containing kaolins from different deposits, which has made it possible to stabilize the technological properties of ceramic mixtures. Thus the use of Glukhovetskoe dry-concentration kaolin mixed with Prosyanovskoe kaolin has improved the casting properties of slips without increasing the quantity of added electrolytes. The dry-concentration kaolin from the Glukhovetskoe deposit has a more stable content of finely-dispersed sand than Prosyanovskoe dry-concentration kaolin. The introduction of 10% Glukhovetskoe kaolin at the expense of decreasing the quantity of Prosyanovskoe kaolin significantly improves the fluidity of slip. The addition of 10 – 15% secondary nonconcentrated Novoselitskoe kaolin into semiporcelain mixtures replacing a part of Glukho-

vetskoe wet-concentration kaolin has improved the casting properties of slips and the quality of preforms, and significantly decreases the industrial waste at the Stroifayans Slavutskii Works and at the Samara Building Ceramics Works.

The Lobnenskii Construction Porcelain Works, the Dulevskii, Bogdanovichskii, Yuzhnouralskii porcelain works, Stroipolimerkeramika JSC (Kaluga Region), and other factories use kaolin from the Zhuravlinyi Log deposit, partly replacing Prosyanosvkoe and Glukhovetskoe kaolin. The liquefiers in this case are water glass, soda, a carbon-alkali reactant, and sodium polyacrylate (PAN-1).

It is known that the use of raw kaolin accelerates the preform wall formation, the mechanical strength of dried articles in this case increases by 10 – 15%, the production waste in casting decreases, and the whiteness of fired articles improves. The producer should have available reserves of concentrated kaolin and milled quartz in order to correct the batch composition, which can be successfully done by using pulverized quartz (marshallite) or ground quartz. Note that many foreign companies use multicomponent ceramic mixtures containing argillaceous components from several deposits, whose share ranges in the limits of 56 – 58%. This makes it possible to impart strictly determined structural-mechanical properties to ceramic mixtures.

An improvement in the properties of ceramic mixtures is observed only when using coarse-grained material produced by moist milling. Short-time dry milling has a positive effect on coarse-grain types of kaolins, whereas excessively long milling has a negative effect.

The methods of mechanochemical and electric-pulse treatment of mineral and ceramic materials is gaining wide acceptance in the development of contemporary technologies. Mechanical activation can substantially improve the liquescence and casting properties of porcelain mixtures and lower their molding properties, as well as improve the mixture sensitivity to drying. At the same time, the effect of mechanical activation on sintering is always highly effective. Therefore, it can be stated that the choice of equipment for milling and preparing suspensions and the mechanical activation conditions to a great extent determine the quality of ceramics articles.

The mechanical activation of initial raw materials in an aqueous medium has a substantial effect on the phase formation processes under thermal treatment of ceramics mixtures. It has been found that treatment of Kyshtymskoe kaolin in an alkaline medium (pH = 10) improves its characteristics and raises the activity of mullitization and cristobalitization processes in aluminosilicate ceramics, substantially decreasing the firing temperature. The mechanical activation of kaolin increases its dispersion by increasing the fraction of particles of size from 10 to 2 μm and also raises the working moisture content, the plasticity number, and air shrinkage, which may complicate the technological process. However, mechanical activation of kaolins can impair the liquescence and filtration

properties of kaolin and porcelain suspensions. In this case it will be necessary to increase the consumption of electrolyte used to obtain a slip. The negative effect of mechanical activation can be eliminated by strict compliance with the technological regulations for each specific material.

Due to mechanical activation of kaolin, the bending strength of samples in the air-dry state grows up to 1.6 – 1.7 MPa, i.e., by 39 – 57%. The strength of ceramic mixtures based on mechanically activated kaolins containing strengthening additives (wood-processing industrial waste, carboxymethylcellulose (CMS)) in the air-dry state exceeds the mechanical strength of initial mixtures by 0.3 – 0.6 MPa. The plasticity number of ceramic mixtures prepared using CMC and based on mechanically activated kaolins increases by about 2 – 4%.

Thus, the quality of ceramics significantly depends on the quality of materials used and their chemical and mineral compositions.

The problem of improving the quality of ceramic materials can be solved by the joint efforts of companies supplying material components and companies producing ceramics. The former should organize selective mining in quarries and use up-to-date concentration methods. The latter should apply the results of researchers and the experience of the leading ceramic companies to successfully controlling technological processes in order to obtain finished products satisfying contemporary requirements.

REFERENCES

1. I. Ya. Yurchak, "The quality of argillaceous materials and whiteness of porcelain products," in: *Publ. of GIKI Institute, Issue 1* [in Russian], Leningrad (1964), pp. 3 – 13.

2. A. É. Énglund, *Rational Consumption of Raw Materials in Porcelain and Faience Industry* [in Russian], Legprombytizdat, Moscow (1986).

3. N. F. Solodkii, *Eluvial Kaolins of the Zhuravlinyi Log Deposit as a New Source of High-Quality Material for Fine Ceramics, Ser. Ceramic Industry, Issue 3* [in Russian], VNIIÉSM, Moscow (1995).

4. V. P. Petrov (ed.), *Nonmetallic Minerals in the USSR. A Reference Book* [in Russian], Nedra, Moscow (1984).

5. G. V. Kukolev, I. Ya. Piven', and V. S. Polishchuk, "The effect of moist milling of materials in ball mills," *Steklo Keram.*, No. 4, 21 – 22 (1972).

6. V. V. Glasson, "The development of an accelerated method for controlling the dispersion and technological properties of argillaceous materials," in: *Porcelain – Faience, Coll. Works of GIKI Institute, No. 2* [in Russian], Leningrad (1962).

7. G. N. Maslennikova, Yu. T. Platov, and R. G. Khalilulova, "The whiteness of porcelain," *Steklo Keram.*, No. 2, 13 – 16 (1994).

8. E. K. Ivanova, "The regulation of the colloid state of kaolin as the main component of fine-ceramic mixtures," in: *New Trends in Porcelain and Faience Technologies* [in Russian], Kiev (1960), pp. 209 – 234.

9. A. V. Éminov and N. N. Zendrikov, "The correlation of the properties of kaolins with their degree of crystallinity," *Steklo Keram.*, No. 7, 20 – 21 (1984).

10. G. I. Kovalev and D. I. Levin, "The specifics of kaolins differing in their degree of crystallinity of kaolinite," in: *Publ. of GIKI Institute* [in Russian], Leningrad (1978), pp. 3 – 24.

11. A. P. Pyzhova, A. V. Gritsenko, and Z. Ya. Kovaleva, "The effect of casting on the modification of the flow properties of Alekseevskoe kaolin treated with polyacrylamide," in: *Publ. of TsNIITÉI Institute* [in Russian], Moscow (1985), pp. 29 – 34.

12. A. P. Pyzhova, V. V. Korobkina, and V. S. Kosov, *The Defects of Fine-Ceramic Articles* [in Russian], Legprombytizdat, Moscow (1993).

13. G. N. Maslennikova, N. F. Solodkii, M. N. Solodkaya, and A. S. Shamrikov, "The use of kaolins from different deposits in fine ceramics," in: *Ceramic Materials: Production and Use, Proc. Sci.-Pract. Conf.* [in Russian], Moscow (2003), pp. 70 – 71.

14. G. N. Maslennikova, N. V. Kolyshkina, A. S. Shamrikov, and Z. V. Stafeeva, "Concentrated kaolin from the Zhuravlinyi Log deposit for ceramic production," *Steklo Keram.*, No. 1, 15 – 19 (2002).

15. N. F. Solodkii, M. N. Solodkaya, and A. S. Shamrikov, "The use of kaolin from the Zhuravlinyi Log deposit in the production of fine ceramics," *Ogneup. Tekh. Keram.*, No. 5, 34 – 35 (2000).

16. N. F. Solodkii, M. N. Solodkaya, and A. S. Shamrikov, "The qualitative characteristic of the technological properties of kaolins from the CIS deposits," *Ogneup. Tekh. Keram.*, No. 10, 32 – 37 (2000).

17. V. N. Antsiferov, A. V. Evstyunin, and S. E. Porozova, "Kaolins from the Prosyanovskoe and Kyshtymskoe deposits as materials for the synthesis of cordierite," *Ogneupory*, No. 7, 27 – 29 (1995).

18. I. I. Moroz, M. S. Komskaya, and L. A. Oleinikova, *Reference Book on Porcelain and Faience Industry, Vol. 2* [in Russian], Legkaya Industriya, Moscow (1980).